

BUNDESREPUBLIK DEUTSCHLAND

DEUTSCHES PATENTAMT

German  
Patent OfficeOpen Laying Document  
DE 36 32 030 A1

Int Cl:

A 61 K 7/11

File Number: P 36 32 030.7  
Application Date: 09/20/86  
Publication Date: 03/31/88

Applicant:  
Wella AG, 6100 Darmstadt, DE

Inventor:  
Lang, Günther, Dr., 6107 Rheinheim, DE;  
Gross, Paul, 6100 Darmstadt, DE;  
Heinrich, Hans, 6806 Viernheim, DE;  
Grundmann, Karin, 6102 Pfungstadt, DE

## Thickened cosmetic media for stabilizing a hairstyle

The invention is concerned with a cosmetic media to be used for stabilizing a hairstyle, and said media is present in the form of a thickened, homogenous aqueous, or aqueous alcoholic preparation that is based on 0.05 to 4 weight percentages of a film creating resin that possesses a molecular weight of 2,000 to 200,000, and that has a content of (a) 0.1 to 4 weight percentages of a high molecular, non-ionic polymer of the group of the cellulose -, chitin -, or chitosan ethers that have a median molecular weight of at least 250,000,

and,

(b) 0.05 to 2.5 weight percentages of a high molecular, cationic polymer that either belongs to the group of the cellulose -, guar -, chitin -, or chitosan derivatives, and that possesses a median molecular weight of at least 300,000, or of the group of the cationic acylamide copolymers with a median molecular weight of at least 800,000, with which the mixing relation between the non-ionic polymer (a), and the cationic polymer (b) is selected in such a manner that the viscosity of the substance that consists of a mixture of (a) and (b) is larger than the viscosity of a substance that possesses a total amount of (a) and (b) in relation to the content of the higher viscous one of the two polymers.

## Patent Claims

1. Cosmetic substance in the form of a thickened, homogenous, aqueous, or aqueous alcoholic preparation for stabilizing a hairstyle that is based on 0.05 to 4 weight percentages of a film creating resin that possesses a median molecular weight of 2,000 to 200,000, **characterized in such a manner** that it contains

(a) 0.1 to 4 weight percentages of a high molecular, non-ionic polymer of the group of the cellulose -, chitin -, or chitosan ethers that have a median molecular weight of at least 250,000, and,

(b) 0.05 to 2.5 weight percentages of a high molecular, cationic polymer that either belongs to the group of the cellulose -, guar -, chitin -, or chitosan derivatives, and that possesses a median molecular weight of at least 300,000, or of the group of the cationic acrylamid copolymer with a median molecular weight of at least 800,000,

with which the mixing relation between the non-ionic polymer (a), and the cationic polymer (b) is selected in such a manner that the viscosity of the substance that consists of a mixture of (a) and (b) is larger than the viscosity of a substance that possesses a total amount of (a) and (b) in relation to the content of the one with a higher viscose of the two polymers.

2. Substance according to claim 1, **characterized in such a manner** that the non-ionic polymer, and that the cationic polymer are present in a mixing relation of 20 : 1 through 1 : 20.
3. Substance according to the claims 1 or 2, **characterized in such a manner** that the amount of non-ionic polymer (a) that is contained in it, and the cationic polymer (b) have been selected in such a way that

$$\frac{X_1}{(X_1 + X_2)} \leq \frac{2\eta_1}{(\eta_1 + \eta_2)}$$

will apply,

with which represents

- |          |   |
|----------|---|
| $X_1$    | the amount of the one of the two polymers that possesses the lower viscosity  |
| $X_2$    | the amount of the two polymers that possesses the higher viscosity  |
| $\eta_1$ | the viscosity of a solution that has a content equals $(X_1 + X_2)$ of the two polymers that possesses the lower viscosity  |
| $\eta_2$ | the viscosity of a solution that has a content equals $(X_1 + X_2)$ of the two polymers that possesses the higher viscosity |

in the relevant solution or solution mixture that is determined by the cosmetic substance.

4. Substance according to the claims 1 through 3, **characterized in such a manner** that the non-ionic polymer of the component (a) is selected from hydroxy ethyl cellulose, hydroxy propyl cellulose, hydroxy propyl methyl cellulose, hydroxy butyl

- methyl cellulose, hydroxy ethyl chitin, hydroxy propyl chitin, hydroxy butyl chitin, hydroxy ethyl chitosan, hydroxy propyl chitosan, hydroxy butyl chitosan.
5. Substance according to the claims 1 through 4, **characterized in such a manner** that the cationic polymer of the component (b) is selected from quaternarydized hydroxy ethyl cellulose, quaternarydized hydroxy propyl cellulose, quaternarydized hydroxy ethyl chitin, quaternarydized hydroxy ethyl chitin, quaternarydized hydroxy butyl chitin, quaternarydized chitosan derivations, following the EP – OS 01 15 574, DE – OS 35 01 891, DE – OS 35 02 833, and DE – OS 35 13 277, as well as acrylamid beta methacrylic oxytrimethyl ammonium chloride co-polymerisates.
  6. Substance according to the claims 1 through 5, **characterized in such a manner** that it contains additionally a cosmetic hair dye with a concentration of 0.01 to 2.0 weight percentages, and that said dye is present in the form of a color fixative or a dye fastener.
  7. Substance according to the claims 1 through 6, **characterized in such a manner** that pH value ranges between 2 and 11.
  8. Substance according to the claims 1 through 7, **characterized in such a manner** that it possesses a tenside or surfactant content of less than 0.4 weight percentages.
  9. Substance according to the claims 1 through 8, **characterized in such a manner** that it possesses a viscosity of at least 200 mPa x s.

#### Description

The invention is concerned with a thickened cosmetic substance that is to be used for stabilizing the hairstyle, and said substance possesses a content of certain non-ionic and cationic polymers.

Substances that are to be used to stabilize a hairstyle consist commonly of aqueous, or aqueous alcoholic solutions of film forming natural and synthetic polymers.

Such liquid hairstyle stabilizers that could also be available in the form of so called blow drying lotions or blow drying stabilizers, however, have the disadvantage that they flow away from the hair easily because of their low viscosity. This results in undesired side effects such as irritation of the eyes, or of sensitive skin areas, soiling of the clothes of the user, or a poor ability to distribute them well caused by the stabilizers flowing away from the manageability and feelings and the hair during its application.

These disadvantages can be reduced by means of increasing the viscosity of such substances, for example by means of adding high molecular compounds, so called thickeners to said substances.

However, some of such thickening processes that are conducted with the support of polymers lead very often to other disadvantages. For example, the algaenates or carboxy methyl cellulose that are most commonly utilized for the thickening process, are not compatible with many important cosmetic substances, specifically not with cationic tenside or surfactants and polymers. Furthermore, they do not dissolve well in alcohol and organic solvents, and thus, their suitability will be limited additionally. Finally, the cosmetic characteristics of the hair, such as being able to be combed easily and its feel were worsened by the anionic polymers due to their negative charge, and this has a specifically negative effect on damaged hair.

It is possible to partially avoid occurring problems concerning the ability to dissolve, as well as the compatibility with other active cosmetic substances by means of utilizing non-ionic polymers, such as, for example, hydroxyalkyl cellulose for the anionic thickening agent. However, the concentrations of such non-ionic polymers that are required for an adequate thickening are so high that it is impossible to avoid causing a burden to the hair. Furthermore, caused by the application of non-ionic polymers, the cosmetic characteristics of the hair will be as negatively influenced as is the case with the application of anionic polymers.

Furthermore, it is possible to utilize cationic polymers such as, for example, cellulose, chitin, or chitosan derivatives as be thickening agents for the stabilization of hairstyles. The hair will also heavily burdened with the utilization of cationic polymers, specifically for those cases in which they are used repeatedly. This is because of the fact that the concentrations that are required for the thickening are also very high. Furthermore, because of the high costs it is very difficult to justify a thickening with cationic polymers due to economical reasons, and on the other side, the durability of hairstyles that are stabilized in such a manner is not satisfactory during periods of high humidity due to the hygroscopic characteristics of the cationic polymers.

Surprisingly, it was now discovered that the above described disadvantages can be avoided by means of utilizing a synergic combination of suitable non-ionic and cationic polymers that are to be used as thickening agents.

10. Thus, the subject of the presented invention is a substance to be used for the stabilization of a hairstyle, and said substance is present in a thickened, homogenous, aqueous, or aqueous alcoholic preparation that is based on 0.05 to 4 weight percentages of a film forming resin that possesses a median molecular weight of 2,000 to 200,000, that is characterized in such a way that it contains
- (a) 0.1 to 4 weight percentages of a high molecular, non-ionic polymer of the group of cellulose -, chitin -, or chitosan ethers that have a median molecular weight of at least 250,000, and,
  - (b) 0.05 to 2.5 weight percentages of a high molecular, cationic polymer that either belongs to the group of the cellulose -, guar -, chitin -, or chitosan derivatives, and that possesses a median molecular weight of at least 300,000, or of the group of the cationic acrylamid copolymers with a median molecular weight of at least 800,000,

with which the mixing relation between the non-ionic polymer (a), and the cationic polymer (b) is selected in such a manner that the viscosity of the substance that consists of a mixture of (a) and (b) is larger than the viscosity of a substance that possesses a total amount of (a) and (b) in relation to the content of the higher viscous one of the two polymers.

The cosmetic substance that is to be used for the stabilization of a hairstyle, and that contains a synergic combination of suitable non-ionic and cationic polymers, is commonly available in the form of an aqueous, or aqueous alcoholic, viscous solution that possesses a minimal viscosity of 200 mPa x s (measured with the support of a Höppler viscosity scale, and the utilization of rod 2 at 30 degrees Celsius and an application weight of 10g).

The substance for the stabilization of a hairstyle that is produced following the invention generally contains film forming, natural or synthetic resins that possess a molecular weight of 2,000 to 200,000, such as, for example, shellac chitosan, polyvinyl pyrrolidone, polyvinyl acetate, polyacrylic compounds, such as, for example acrylic acid, and methacrylic acid polymerisates, or basic polymerisates of esters of acrylic acid, or methacrylic acid with amino carbons, polyacrylic nitril, as well as co and terpolymerisates of such compounds, such as, for example, polyvinyl pyrrolidone vinyl acetate in an amount of 0.05 to 4 weight percentages.

The non-ionic polymers of the component (a) that are utilized in the substance that is produced following the invention possess a molecular weight of at least 250,000, and they specifically consist of non ionogenic celluloses, chitin, or chitosan derivatives, such as, for example hydroxy ethyl cellulose, hydroxy propyl cellulose, hydroxy propyl methyl cellulose, hydroxy butyl methyl cellulose, hydroxy ethyl chitin, hydroxy propyl chitin, hydroxy butyl chitin, hydroxy ethyl chitosan, hydroxy propyl chitosan, hydroxy butyl chitosan.

Suitable cationic polymers of the component (b) are cationic polysaccharid derivatives that possess a median molecular weight of at least 300,000, or synthetic cationic polymers that possess a median molecular weight of at least 800 000. Considered as suitable polysaccharid derivatives are cationic cellulose derivatives, such as, for example, quaternarydized hydroxy ethyl cellulose, and quaternarydized hydroxy propyl cellulose, quaternarydized guar derivatives, quaternarydized chitin derivatives, such as, for example, quaternarydized hydroxy ethyl chitin, quaternarydized hydroxy butyl chitin, as well as quaternarydized chitosan derivatives, such as they have been described, for example, in the own EP – OS 01 15 574, DE – OS 35 01 891, as well as in our own published German patent applications DE – OS 35 02 833, and DE – OS 35 13 277. Considered to be suitable as synthetic cationic polymers are, for example, cationic acrylamid copolymerisates, such as, for example, acrylamid beta methacrylic oxytrimethyl ammonium chloride co-polymerisates [the name of this compound is "Polyquaternium-15" according to CTFA Cosmetic Ingredient Dictionary 3<sup>rd</sup> Edition, Supplement (1985)].

The suitable mixing relation of non-ionic and cationic polymers can vary depending on the preparation and the type of the utilized non-ionic and cationic polymer, and it can range between 1 : 20, and 20 : 1. For the hydroxypropyl cellulose that is utilized as the component (a) in the examples 2 through 4, as well as for the quaternarydized hydroxyethyl celluloses that is used as the component (b) the relation following the invention is, for example, 8 : 1 through 2 : 1.

However, one requirement is the presence of a synergetic thickening action. Because of this fact, it is imminent that the amount of the non-ionic and cationic polymer that is contained in the substance that is executed according to the invention is selected in such a manner that

$$\frac{X_1}{(X_1 + X_2)} \leq \frac{2\eta_1}{(\eta_1 + \eta_2)}$$

will apply,

with which represents

- $X_1$  the amount of one of the two polymers that possess the lower viscosity
- $X_2$  the amount of two polymers that possess the higher viscosity
- $\eta_1$  the viscosity of a solution that has a content equals  $(X_1 + X_2)$  of the two polymers that possesses the lower viscosity
- $\eta_2$  the viscosity of a solution that has a content equals  $(X_1 + X_2)$  of the two polymers that possesses the higher viscosity

in the relevant solution or solution mixture that is determined by the cosmetic substance.

A substance with a content of a non-ionic and a cationic polymer, with which the mixing relation between the two polymers is selected in such a way that it possesses a lower or identical viscosity as it would have if it would contain only one of the two polymers in a total amount of  $(X_1 + X_2)$  thickened substance is thus not the subject of the presented patent application.

The film forming resin, as well as the non-ionic polymer (a), and the cationic polymer (b) can each consist of a single substance as well as of an unspecified mixture that consists of several substances of the stated kind.

The substance that is produced according to the invention preferably possesses a pH value that ranges between 2 and 11, and it can be present in the shape of a thickened, homogenous, aqueous, or aqueous alcoholic preparation, preferably in the form of a solution, cream, gel, or emulsion.

Specifically suitable to be considered herewith as alcohols are the lower alcohols that are commonly utilized for cosmetic purposes, and that possess 1 to 4 carbon atoms, such as, for example, ethanol and isopropanol.

Additionally, it is possible that the substance that is produced according to the invention, and that is to be utilized for the stabilization of a hairstyle, can contain the additives that are common for such kinds of substances. These additives could be, for example, perfume oils, conserving agents, anti dandruff agents, enhancing substances for easy hair combing, such as, for example, quaternary ammonia salts, modifying agents, such as, for example, silicon oil, moisturizers, such as, for example, glycerin, or propylen glycol, cosmetic oils, stabilizers, pigments, clouding agents, solvent enhancing agents, sequestering agents, fatty alcohols, waxes, buffering agents, or emulgation agents, as well as hair care components, such as, for example, lanolin derivatives, cholesterol, pantothen acid or batin.

The substance that is produced according to the invention and that is to be used for stabilizing a hairstyle could at the same time dye or color the hair by means of a content of cosmetic hair dyes. Preparation of such kinds are commonly called color enhancers or dye stabilizers. In addition to the hair stabilizer they contain the common and known cosmetic hair dyes that can be applied directly to the hair, such as, for example aromatic nitro dyes (for example, 1,4-diamino-2-nitro-benzol, pikramin acid, 1-hydroxy-2-amino-4-nitro-benzol, and 1,4-bis-[(2-hydroxy ethyl)-amino]-2-nitro-5-chlorin-benzol, azo dyes 9 for example, C. 1. 14 805 – Acid Brown 4), anthrachinon dyes (for example, C. 1. 61 105 – Disperse Violet 4), and triphenyl methane dyes (for example, C. 1. 42 535 – Basic

Violet 1), with which the dyes of these classes can possess, depending on their kind of substitutes, either an acid, non-ionic, or basic characteristic. Their total concentration in the substance that is produced according to the invention ranges commonly around 0.01 to 2.0 weight percentages.

The substance that is produced according to the invention and that is to be used for stabilizing a hairstyle, and that is based on a mixture of a non-ionic and a cationic polymer possesses the advantage that the viscosity that is required for an optimal utilization can be achieved by means of a small amount of thickening agent, and because of this, the burden for the hair will be reduced. This function is possible due to the synergistic thickening action of the two polymers. Furthermore, as it can be seen from the following comparison examples, the cosmetic characteristics of the hair, as for example, the ability to comb it easily, manageability and feeling, and stability of the hairstyle will be improved tremendously, as well as the ability to distribute the substance and the flow away characteristics of the substance if this is compared with the common hairstyle stabilizers that are thickened with the support of anionic, cationic, or non-ionic polymers.

The following examples shall explain the object of the invention in more detail without creating a limitation to said examples for it.

## Examples 1 through 6

## Thickened liquid substances for stabilizing a hairstyle

	Examples					
	1	2	3	4	5	6
Hydroxypropyl cellulose, MW ~ 1 000 000 (Klucel H, Hercules Inc.)	1.0	0.875	0.75	0.625	0.25	-
Quaternarydized hydroxy ethyl cellulose following US PD 34 72 840, MW ~ 750 000 (Polymer JR-30 M, Union Carbide Corporation)	-	0.125	0.25	0.375	0.75	1.0
Ethanol	40.0	40.000	40.00	40.000	40.00	40.0
Vinyl acetate croton acid ethylene oxide, MW ~ 100 000 (Aristoflex A, Hoechst Aktiengesellschaft)	2.0	2.000	2.00	2.000	2.00	2.0
Perfume oil and dye	0.5	0.500	0.50	0.500	0.50	0.5
Water	56.5	56.500	56.50	56.500	56.50	56.5
(Statements in weight percentages)	100.0	100.000	100.00	100.000	100.00	100.0
Viscosity [mPa x s]	1040	2040	2100	1880	990	550

The examples 2 through 4 clearly demonstrate the synergetic increase of the viscosity that is caused by suitable combinations of cationic and non-ionic polymers if compared to a thickening with the identical amount of only one of the two polymers (example 1 and 6).

The comparison example 5 possesses a viscosity that is lower than the one in example 1, and thus, it is positioned outside of the range of the invention.

Eight (8) g of the relevant hair stabilizer that is made according to the examples 1 through 6 will be applied to towel dried hair, they will be distributed in the hair, and they will be dried in the common fashion while rolled onto water curlers. The following results are obtained subsequent to the removal of the curlers:



---

	Example					
	1	2	3	4	5	6
Ability to comb (wet)	-	+	++	+	+	+
Static charge	(a)	(b)	(b)	(b)	(b)	(b)
Manageability and feeling in dried condition	-	+	+	+	(c)	(c)
Stability of the hairstyle under humid conditions	+	+	+	+	-	-

Herewith means:

- = bad, + = good, ++ = very good

(s) = strong, (b) = low, (c) = burdened

## Examples 7 through 12

## Blow drying stabilizers

	Examples					
	7	8	9	10	11	12
Hydroxy propyl cellulose, MW ~ 1 000 000 (substitution degree: methyl 2.0; hydroxy butyl 3.0) (Methocel HB, Dow Chemical Company)	1.0	0.5	0.625	0.75	-	-
Quaternarydized hydroxy ethyl cellulose following US PD 34 72 840, MW ~ 750 000 (Polymer JR-30 M, Union Carbide Corporation)	-	0.5	0.375	0.25	1.0	-
Ethanol	45.0	45.0	45.000	45.00	45.0	20.00
Vinyl acetate croton acid ethylene oxide, MW ~ 100 000 (Aristoflex A, Hoechst Aktiengesellschaft)	1.0	1.0	1.000	1.00	1.0	-
Polyacrylic acid, MW ~ 400 00 (Carbopol 940, BF Goodrich Company)	-	-	-	-	-	0.40
Ammonia (25 percent aqueous solution)	-	-	-	-	-	0.32
Polyvinyl pyrrolidon vinyl acetate copolymer, MW ~ 40 00 (40 percent isopropanol solution ) (Luviskol VA 37I; BASF Aktiengesellschaft)	-	-	-	-	-	3.00
Cetyl trimethyl ammonia chloride (20 percent aqueous solution)	0.1	0.1	0.100	0.10	0.1	-
Perfume oil and dye	0.5	0.5	0.500	0.50	0.5	0.50
Water	52.4	52.4	52.400	52.40	52.4	75.78

(Statements in weight percentages)	100.0	100.0	100.000	100.00	100.0	100.00
Viscosity [mPa x s]	520	750	900	850	498	950

Six (6) g of the relevant hair stabilizer that is made according to the examples 7 through 12 will be applied to towel dried hair. The hairstyle will be created with the support of a hair dryer and a brush. The results concerning the most important application technological criteria are compiled in the following table:

	Example					
	7	8	9	10	11	12
Ability to comb	-	+	+	+	+	--
Gliding ability of the brush	-	+	+	+	+	--
Shaping of a hairstyle	++	++	++	++	++	+
Static charge	(a)	(b)	(b)	(b)	(b)	(c)
Manageability and feeling, dry	+/-	+	+	+	+	-
Stability of the hairstyle under humid conditions	+	+	+	+	+/-	+/-

Herewith means:

-- = very bad, - = bad,

++ = very good + = good, +/- = marginal

(a) = strong, (b) = low,

(c) = very strong

The table displays the supremacy of the examples 8 through 10 that are obtained with the substance that is made according to the invention in comparison to the comparison examples 7 (pure non-ionic), 11 (pure cationic), and 12 (thickened in a conventional manner).

## Examples 13 through 18

## Color stabilizers

	Examples					
	13	14	15	16	17	18
Hydroxypropyl cellulose, MW ~ 1 000 000 (Substitution degree: methyl 1.3; hydroxy propyl 0.82) (Methocel J 75 MS, Dow Chemical Company)	0.80	0.80	1.60	1.60	-	-
Quaternarydized hydroxy ethyl cellulose following US PD 34 72 840, MW ~ 750 000 (Polymer JR-30 M, Union Carbide Corporation)	0.30	0.30	-	-	-	-
Polyvinyl pyrrolidon vinyl acetate copolymer, MW ~ 40 00 (40 percent isopropanol solution ) (Luviskol VA 37I; BASF Aktiengesellschaft)	4.00	4.00	4.00	4.00	6.00	6.00
Isopropanol	30.00	30.00	30.00	30.00	30.00	30.00
Acid Brown 4 (C. I. 41 805)	0.05	-	0.05	-	0.05	-
1,4-bis-(2-hydroxy ethyl)-amino-2-nitro-5chlorid benzol	-	0.15	-	0.15	-	0.15
Perfume oil	0.30	0.30	0.30	0.30	0.30	0.30
Water	64.55	64.55	64.05	63.95	63.65	63.55
(Statements in weight percentages)	100.00	100.00	100.00	100.00	100.00	100.00
Viscosity [mPa x s]	1700	1700	1600	1600	thin liquit	thin liquit

Ten (10) g of the relevant substance will be distributed onto the washed and towel dried hair. Following this process, the hair will be dried and the hairstyle will be fashioned in the common way. For the case that the substances following example 13, 15 and 17 are utilized, the hair will display a slight red-brown coloration, while a red-violet coloration will be obtained upon the utilization of the examples 14, 16, and 18.

The color stabilizers following the examples 13 through 18 possess a comparable stabilization action while the ability to comb the hair is better with the examples 13 and 14 that are produced according to the invention than it is with the comparison examples 15, 16, 17, and 18. The examples 17 and 18 display a slight coloration of the scalp that is much lower with the thickened example 13, 14, 15, 16.

All percentage statements in the presented application represent weight percentages.

The determination of the viscosity happens with the support of a ball pull viscosity meter ("Höppler Viskowaage"), and with the utilization of rod 2 at 30 degrees Celsius, and with an application weight of 10 g.

Translated by:  
Dietmar Schlei  
(715) 386-5779  
(612) 736-2057